Synthesis of Ceria Nanopowder for the removal of Hexavalent Chromium from synthetic Cr (VI) solution

A Dissertation

Submitted in partial fulfilment for the degree of

MASTER OF SCIENCE IN CHEMISTRY

By

Miss Shilpa Jena

UNDER THE SUPERVISION

Of

Prof. RAJ KISHORE PATEL

Department of chemistry, National institute of Technology,

Rourkela -769008

Declaration

The work embodied in this report is an original investigation carried out by the author, on the topic entitled, ***"Synthesis of Ceria Nanopowder for the removal of hexavalent chromium from synthetic Cr (VI) solution"****, for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.*

Shilpa Jena

Department of Chemistry

National Institute of Technology,

ROURKELA, Odisha,

India 769008

CERTIFICATE

This is to certify that the project report entitled, "***Synthesis of Ceria Nanopowder for the removal of hexavalent chromium from synthetic Cr (VI) solution***", is being submitted to National Institute of Technology, Rourkela by Ms. Shilpa Jena, Roll number 410cy2013 for partial fulfilment of the Master of Science degree, Chemistry, which is an original work carried out under my guidance and supervision. This work has not been submitted by him for any other degree to any other Institution or University.

The present study is a valuable contribution for the advancement of knowledge in the field of material chemistry and its environmental application.

In habit and character Ms. Shilpa Jena is quite a fit and proper person for the further research work.

I wish her all success in his future life.

Prof. R.K. PATEL

Department of chemistry

NIT-Rourkela

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I express my heartfelt thanks to Dr. B.G. Mishra, HOD, department of chemistry, NIT-Rourkela, for giving me an opportunity to carry out project work, thus helping me in taking the first step towards research. I acknowledge the assistance provided by Environmental Lab research scholar Mr Sandip Mandal during experimental study.

Last but not the least; I am indeed indebted to my parents whose understanding attitude, constant inspiration and patience to listen to my difficulties kept me in high spirits for completing this work.

Shilpa Jena

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ABSTRACT

Hexavalent chromium is a toxic form of chromium metal generally used in many industrial applications for its anticorrosive properties. Removal of chromium from water is obligatory in order to avoid the chromium contamination. From literature review it is found that water containing hexavalent chromium causes severe health problems throughout the world. There are several methods like chemical precipitation, electro-dialysis, photo-catalysis, ion exchange method, activated carbon adsorption or bio sorption, solvent extraction, reverse osmosis. Which are used to remove chromium from the water but they are not feasible in all places and conditions due to various serious limitations. Among all the technique available, adsorption is one of the most suitable because of its useful process. But the efficiency of the process depends on the adsorption media. Though there are several adsorbent available still there are huge scopes to develop a number of adsorption media for the benefit of the common people. In this work the Ceria nanopowder is synthesized by using Cerium chloride and sulphuric acid at a pH of 7, an attempt has been made to remove the chromate by Ceria nanopowder in batch mode. The adsorbent is characterized by various analytical techniques like FTIR, SEM, XRD, BET and AAS. The percentage removal of hexavalent chromium was studied as a function of pH of the solution, contact time, dosage of adsorbent and reaction temperature. The removal of chromium from the synthetic solution having initial Cr (VI) concentration of 100 mg/L was found to be 86.4 % at an optimal condition of pH 6, adsorbent dose 0.07mg/100ml, temperature 30^0C and contact time of 30 minutes.

Keywords: Chromium, Adsorption isotherms, XRD, AAS

1. INTRODUCTION

1.1. Environmental effects of chromium:

Chromium is a metal that is widely distributed in the earth's crust, air and water. Naturally occurring chromium is has three stable isotopes ^{52}Cr, ^{53}Cr and ^{54}Cr. It occurs mainly in the chromium (III) form as chromite ore, which contains oxygen, chromium (III) and other metals. Chromium (VI) compounds are produced widely from chromite ore for a wide variety of uses. Chromium exists in air, water and soil, mostly in the trivalent chromium form. This however only applies to trivalent chromium. Hexavalent chromium is very toxic to flora and fauna. The mechanism of toxicity is pH dependent. It is only as a result of human activities that substantial amounts of hexavalent chromium become present. Trivalent chromium compounds are not highly toxic and are an essential nutrient that helps the body to use sugar, protein, fat etc. and shortages may cause heart problems, disruptions of metabolisms and diabetes. But the uptake of too much trivalent chromium can cause health effects as well, for instance skin rashes. Hexavalent chromium compounds are divided up in water hazard class 3, and are considered very toxic. The excessive exposure to dusts or mists of hexavalent chromium compounds produces dermatitis, ulceration and perforation of the nasal septum, as well as liver and kidney damage. With long-term exposure to hexavalent chromium compounds, human lung cancer increases. Breathing high levels of hexavalent chromium can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Skin contact with certain hexavalent chromium compounds can cause skin ulcers. Some people are extremely sensitive to hexavalent chromium or trivalent Chromium. Allergic reactions consisting of severe redness and swelling of the skin have been noted. There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the trivalent chromium and hexavalent chromium form through natural processes and human activities. These applications will mainly increase

concentrations of chromium in water. Through coal combustion chromium ends up in air and through waste disposal chromium will end up in soils. Most of the chromium in air settle and end up in waters or soils. Chromium present in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water chromium will absorb on sediment and become immobile. Only a small part of the chromium compound that ends up in water will eventually dissolve. Trivalent chromium is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Hexavalent chromium is mainly toxic to organisms. It has a property to alter genetic materials and cause cancer. Crops have specific systems that can arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only Trivalent Chromium. This may be the essential kind of chromium, but when concentrations exceed a certain value, the negative effects also still occur. Chromium does not accumulate in the bodies of fish, but at very high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that present near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, infertility and tumour formation. Chromium phytotoxicity is undetermined. At concentrations of between 600 and 5000 ppm in soils, plants were not damaged. Lime or phosphate in soils further decreases the chromium susceptibility. Air-dried soil usually contains 2-100 ppm of chromium. Chromium solubility in soil water is lower than that of other potentially toxic metals. This explains the relatively low plant uptake. Under normal conditions plants contain approximately 0.01-1 ppm of chromium, although values may increase to 14 ppm.

1.2 Chromium related Health hazard:

The human body contains approximately 0.02 ppm of chromium. Daily intake into the body strongly depends upon feed levels, and is approximately 15-200 μg. Chromium uptake Upto 0.5-1%, in other words is very small. The placenta is the organ with the highest chromium amounts. People exposed to chromium through eating, drinking, and breathing and through skin contact with chromium. Trivalent chromium is an essential element for humans. It along with insulin removes glucose from blood, and also plays a fundamental role in fat metabolism. Chromium deficits then develop diabetes symptoms. Chromium in some cases can also be found in RNA. Chromium deficits are unusual, and chromium feed supplements are not often applicable. Trivalent Chromium toxicity is not so significant, at least when it is taken up through food and drinking water. It may even improve health, and also cure neuropathy and encephalopathy. Hexavalent chromium is important for its negative health and environmental impact, and its extreme toxicity. Chronic inhalation of hexavalent chromium has been shown to increase risk of lung cancer and may also damage the small capillaries in kidneys and intestines. Other adverse health effects related to hexavalent chromium exposure, according to the National Institute for Occupational Safety and Health (NIOSH), include skin irritation, allergic contact dermatitis, nasal ulceration, perforated nasal septa, nosebleed, respiratory irritation, nasal cancer, eye irritation and damage, kidney damage, pulmonary congestion and edema, epi-gastric pain, and erosion and discoloration of one's teeth. It causes allergic reactions, is carcinogenic and is 1000 times as toxic as trivalent chromium. Health effects related to hexavalent chromium exposure include stomach and intestinal bleedings, liver and kidney damage. Hexavalent chromium has mutagenic effect. Toxic effects are passed on to children through the placenta. Hexavalent chromium oxide is a strong oxidant. Upon dissolution chromic acid is formed, which strongly affects the organs. Most countries apply a permissible limit of 50 ppb chromium in drinking water. A certain

illness in chromium industries is chromium sores upon skin contact with chromates. Hexavalent chromium is a danger to human health, mainly for those people who work in the steel and textile industry. People smoking tobacco also have a higher chance of exposure to chromium. Chromium trioxide dust uptake in the workplace also causes cancer, and damage the respirational tract. The health hazards that are associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is highly toxic for the living organisms. There are various report of adverse effects of the hexavalent form. Because of these health effect, World Health Organisation (WHO), established a guideline of maximum permissible limit which is 1.5 mg/L. Chromium has the following effects on organisms:

- Chromium (VI) compounds are toxic and cause cancer in humans.
- Ingestion of chromium (VI) chromate compounds causes immediate
  Burning of the mouth and severe damage to the gut, liver and kidneys
  and leads to death.
- Short-term inhalation of chromium (VI) chromate dust cause irritation of the respiratory tract and lung damage.
- Long-term inhalation of chromium (III) salts causes swelling of the respiratory pathways and lungs.
- Long-term inhalation of chromium (VI) may cause ulcers in the nose, irritation of the lungs and possible kidney effects.
- Skin exposure to chromium (VI) compounds result in skin ulcers if left untreated.
- Potassium dichromate is toxic to the reproductive system and the unborn child.

1.3 Literature Review

Occurrence:

Chromium is a hard, lustrous, metallic element with an atomic number 24 having silvery white colour and has a high melting point. Chromium is found in the earth crust as a mineral called Crocoite ($PbCrO_4^-$). Chromium is also found as ore in the oxide form called chromite ($FeCr_2O_4$). It is the only ore of chromium found in earth. Chromium is the 21st most abundant element in earth's crust.

Chromium occurs naturally in soil, plants and animals and land erosion causes release of chromium into water. The major sources of chromium (III and VI) in the air, soil and water are through combustion of fossil fuels and from domestic and industrial waste. Hexavalent chromium compounds are toxic at low concentrations for both plants and animals. The main human activities that increase the concentrations of trivalent chromium are steal, leather and textile manufacturing. The main human activities that increase hexavalent chromium concentrations are chemical, electro painting and other hexavalent chromium applications in the industry.

Chromium is a dietary requirement for a number of organisms. Also Chromium (VI) compounds are classified by International Agency for Research on Cancer (IARC) as causing cancer in humans if it is breathed in, whereas chromium (III) compounds could not be classified and are therefore not considered to cause cancer. In the literature, various types of substances are used for the removal of hexavalent chromium. The hexavalent chromium can be removed from water by using bio-sorbents like microorganisms i.e. bacteria, algae, fungi etc. (Bidyut Saha.et.al). The Cr (VI) can be removed by using rice husk and saw dust (Manjeet Bansal.et.al), by using a novel carbon adsorbent (S.B. Lalvani.et.al). Cr (VI) can also remove by using activated carbon (M. J. Owlad.et.al), by using sphagnum moss peat (D.C. Sharma.et.al), from tannery effluent (K.M.S. Sumathi.et.al), by composite chitosan bio-sorbent (Veera M. Boddu.et.al).

In this study, Ceria nanopowder is synthesized by using Cerium chloride and sulphuric acid as starting material. Then ammonium bicarbonate is added and pH is maintained to get the particles of Ceria nanopowder. The synthesized material is then examined by various characterizations techniques like FTIR, XRD, SEM and BET. The synthesized material is used as an adsorbing material under the optimum conditions for adsorption of hexavalent chromium. In this adsorption technique, Ceria nanopowder has successfully reduced the hexavalent chromium concentration. The Ceria nanoparticle on the surface adsorption binds to the chromate and dichromate ions and reduces the chromium concentration.

***Uses*:**

Chromium has a wide variety of applications. Chromium is alloyed with steel to make it corrosion resistant or harder. An example is its use in the production of stainless steel, bright, shining steel that is strong and resistant to oxidation. The production of stainless steel consumes most of the chromium produced annually. Chromium is also used to make heat-resisting steel so called "super-alloys". These super alloys use chromium and have strategic military applications.

Chromium also has some use in the manufacture of certain chemicals. For example, chromium-bearing chemicals are used in the process of preparing leather. Chromium compounds are also used in the textiles industries to produce a yellow colour.

1.4 Adsorption Techniques for Removal of Chromium:

The technique adopted in chromium removal is to adsorb chromium from chromium-bearing aqueous media to a phase that can be separated from the water. A number of methods used for removal of chromium such as membrane techniques, reverse osmosis, Nano-filtration, dialysis, solvent extraction, Nano-filtration and adsorption. The adsorption of Hexavalent chromium by a number of materials such as leaf mould, activated groundnut husk carbon, coconut husk and palm pressed fibres, coconut shell activated carbon, coconut shell, wood

and dust coal activated carbons, coconut jute carbon, coconut tree sawdust carbon, sawdust and used tyres carbon have been reported in the literature. In this study, Ceria Nanopowder have successfully reduced chromium concentration to acceptable levels, surface adsorption, in which chromium is adsorbed on to Ceria nanoparticles, which is of greater accessibility and lower cost, especially in countries where the problem of excessive chromium in available drinking water is very high. Thus even in the past decade, many workers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of all adsorbents. In this report Ceria Nanopowder is used to study the removal of chromium from contaminated water samples through adsorption.

1.5 Aims and Objective of the Present Work:

The present work is carried out with the following objective

A. To synthesis and characterize the Ceria nanopowder.

B. To utilize the material to know the removal efficiency of hexavalent chromium.

C. To find the optimum condition for removal of hexavalent chromium.

D. To formulate a process for field application.

In the context of the above mentioned objectives, there exists a possibility to synthesize and explore the metal adsorption properties of a number of Ceria based adsorbent materials. This is quite important because of the opportunity to synthesize a variety of new Ceria based hybrid materials and their application for metal adsorption.

In our present study, we have prepared Ceria Nanopowder by using Cerium chloride and sulphuric acid. The synthesized Ceria Nanopowder is characterized by spectroscopic techniques and its metal adsorption properties were studied with variation of adsorbent dose, pH and concentration of metal ions etc. using batch adsorption technique.

2. EXPERIMENTAL SECTION

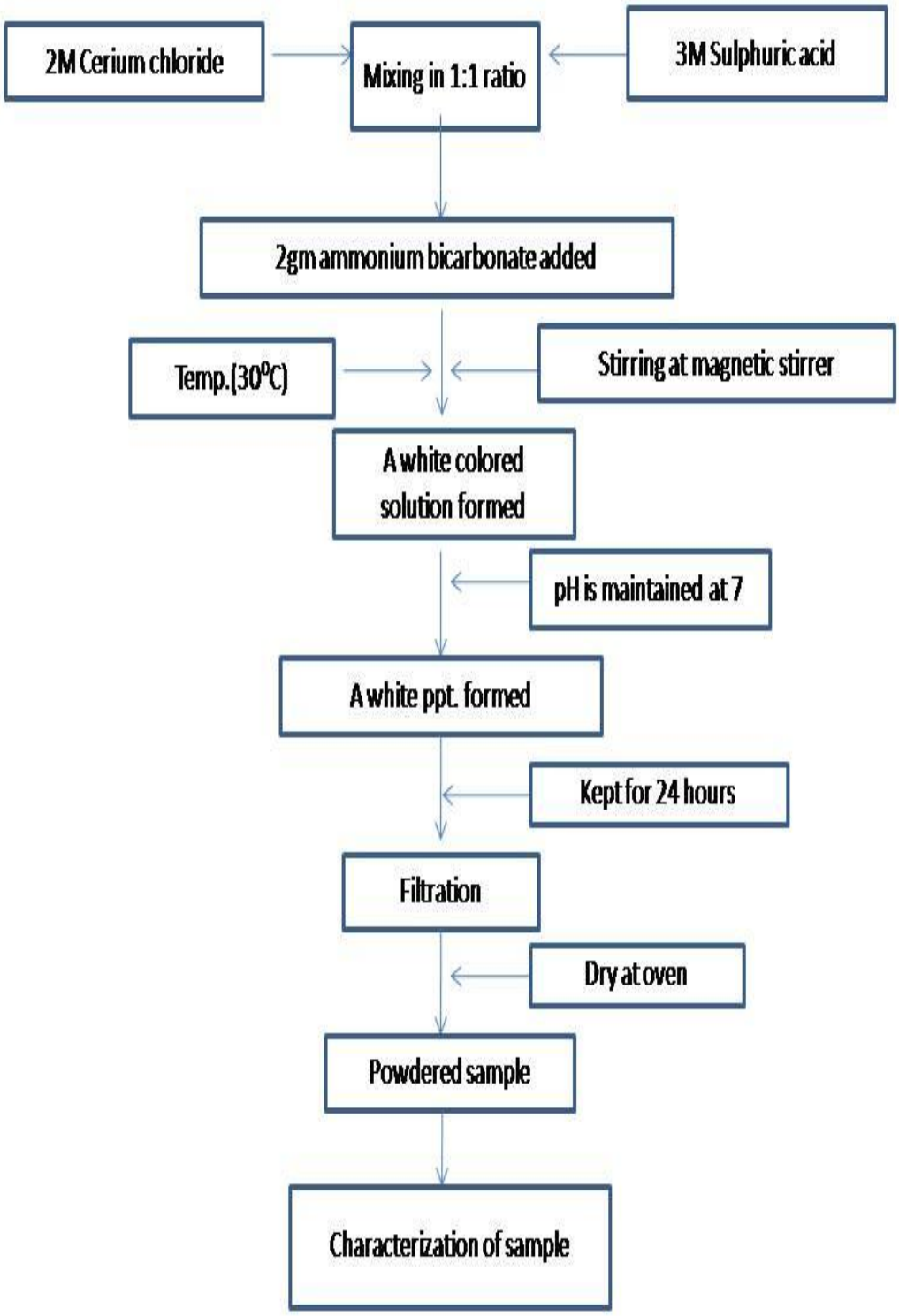
2.1 Materials and Methods

All chemicals used for this study was of AR grade. All glassware like measuring cylinder, volumetric flask, conical flask, etc., was of borosil and tarson. Cerium chloride and Sulphuric acid were used for the synthesis of the nanoparticles. Standard solution of chromium was prepared from potassium chromate (K_2CrO4). Nitric acid (HNO_3) and Ammonium Hydroxide (NH_4OH) were used to vary the pH. The other instruments used in this study are pH meter (Elico), AAS (Perkin Elmer PE Analyst Atomic Absorption Spectroscopy), FTIR, XRD (Phillips Powder Diffract meter Model PW 1830) and SEM (JEOL, jXA-8100***).***

2.2 Synthesis and analysis of Ceria Nanopowder

Ceria Nanopowder was synthesized by mixing aqueous solutions of various concentrations of Cerium chloride and sulphuric acid in 1:1 ratio. First 2M cerium chloride was taken in a beaker and 3M sulphuric acid was taken in a burette. Then 2gm of ammonium bicarbonate is added to the beaker containing cerium chloride solution and placed on a magnetic stirrer with hot plate. The burette containing sulphuric acid is placed over the beaker and sulphuric acid is added drop wise to it and the stirrer is maintained at 300 rpm and 27 ± 2^0c. The desired pH was adjusted by adding required amount of dilute nitric acid or ammonium hydroxide drop wise. The precipitate so obtained was allowed to stand 24 hours at room temperature and was then filtered and washed with distilled water to remove excess reagent till the filtrate attains a pH value of 7. Then it is dried in an oven at a temperature 50^0c for 3 to 4 hours. The materials obtained were kept in an air tight container for further analysis. The chromium concentration was measured by AAS. The X-ray diffraction analyses were done over a range of 10 to 800 using Phillips Powder Diffractometer Model PW 1830.The particle size of the material is analysed to determine its nano order range. The surface morphology of the material were studied using scanning electron microscope (JEOL, jXA-8100).

2.3. Flowchart for preparation of Ceria Nanopowder



2.4: Adsorption experiments

The hexavalent chromium adsorption experiments from its aqueous solution on Ceria nanopowder were carried out using various concentrations of standard Cr (VI) solution in absence of other competing ions. The adsorption experiments were carried out in 250ml glass conical flask with stopper by adding 0.02, 0.04, 0.06, 0.08 and 0.1 g of Ceria nanopowder in 100 ppm (100mg/litre) of hexavalent chromium solution in different adsorbent dose. All the adsorption experiments were carried out at ambient temperature (23±2 ◦C).The conical flasks are placed on the magnetic stirrer for 2 hours. After continuous stirring over the stirrer at about 400 rpm, the solid was separated by filtration through Whatman-42 filter paper and the remaining hexavalent chromium concentration was determined by Perkin- Elmer Atomic Absorption Spectrophotometer (AAS). Measurement was done by taking 10ml of each standard and sample into separate 150ml beaker by standard procedure followed in AAS. All the sample and standards were maintained at same temperature to avoid interference due to difference in temperature. The pH of the solution was maintained when needed, by addition of nitric acid (1.0 N) or ammonium hydroxide solution (1.0 M) and was measured with an Elico pH meter. A number of parameters such as contact time, concentration of adsorbate and pH affecting the removal percentage of chromium ion have been varied widely in order to optimize the adsorption process. The prepared Ceria Nanopowder was used for the adsorption experiments and maximum removal percentage was 86.4%.

3. Result and Discussion

3.1 Characterization of Ceria Nanopowder

The present study is an attempt to explore synthesis of Ceria nanopowder and its application for the removal of hexavalent chromium from synthetic solution. The material is characterized based on the data of analysis of SEM, XRD, FTIR, BET and the report of the similar work. The chemical analysis and elemental analysis of the material is presented in

(Table 1.) the material forms a nano material with very small pores. In order to identify the chemical stability, the material was kept in 30 ml of different mineral acids, bases and salt solutions of different concentration for 12hours and the supernatant liquid was examined for cerium (Table 2). The material reveals moderate chemical stability, and was found that the material was moderate stable in most of the mineral acids and salt solutions. The main physicochemical parameters of the contaminated water are listed in (Table 3).

Table- 1: Chemical properties of present Ceria nanopowder

	N%	*C%*	*H%*	*S%*
Ceria Nanopowder	0.148196	8.01272202	1.72027361	4.08253527

Table-2: chemical stability of the Ceria nanopowder

Solvent (50 ml)	Stability
1M H_2SO_4	Soluble
2M H_2SO_4	Soluble
4M H_2SO_4	Soluble
1M HNO_3	Soluble
2M HNO_3	Soluble
4M HNO_3	Soluble
1M HCL	Soluble
2M HCL	Soluble
4M HCL	Soluble
1M NaOH	Insoluble
2M NaOH	Insoluble
4M NaOH	Insoluble
1M NH_4OH	Insoluble
2M NH_4OH	Insoluble
4M NH_4OH	Soluble

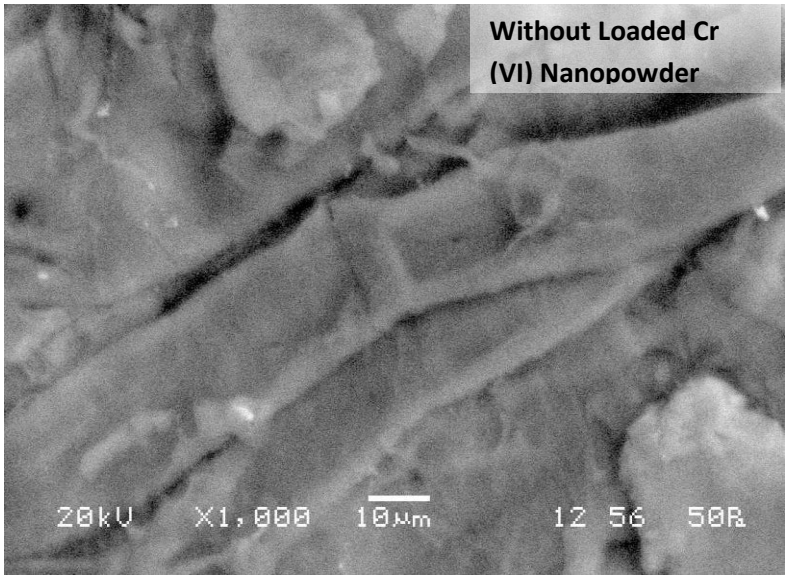
Table- 3: shows the main physicochemical parameters of the contaminated water

Mg^{2+}	56.21 mg/L
Ca^{2+}	121.94 mg/L
TH(Total Hardness)	178.20 mg/L
COD	15.86 mg/L
TOC	0.02 mg/L
Cl^{-}	87.80 mg/L
Fe^{3+}	0.20 mg/L
SO_4^{2-}	71.40 mg/L
NO_3^{2-}	4.70 mg/L
F	0.06 mg/L
Hg^{2+}	NIL mg/L
Cd^{2+}	0.02 mg/L
Cr(VI)	0.007 mg/L
Al^{3+}	0.01 mg/L
Pb^{2+}	0.0001 mg/L
As^{3+}	0.002 mg/L
Cu^{2+}	0.05mg/L

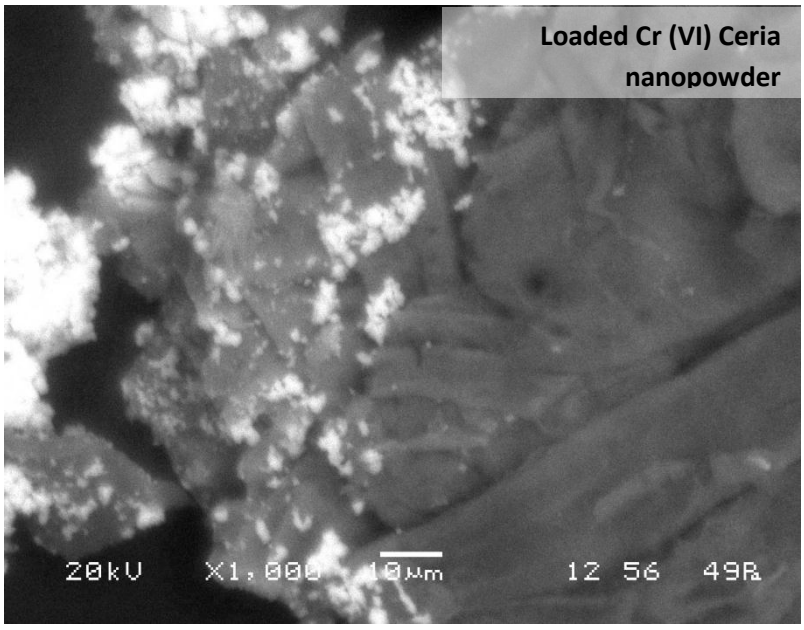
3.1.1 SEM micrographs of Ceria nanopowder

The surface morphology of the material is studied by Scanning electron microscopy (SEM) is presented in (Figure 1). The SEM comparison is done between before adsorption and after adsorption to better understanding of the change in the surface morphology, from Figure 1a i.e. is before adsorption that the material is a having broad fibres and do not have identifiable pores. From figure 1b i.e. after adsorption it is clear that the chromium ions adsorbed on the surface and the surface looks like a white material poured into it. Further for better confirmation EDAX is done, it states that the material was adsorbed hexavalent chromium.

Figure 1: Scanning electron micrographs (SEM) of before adsorption and after adsorption

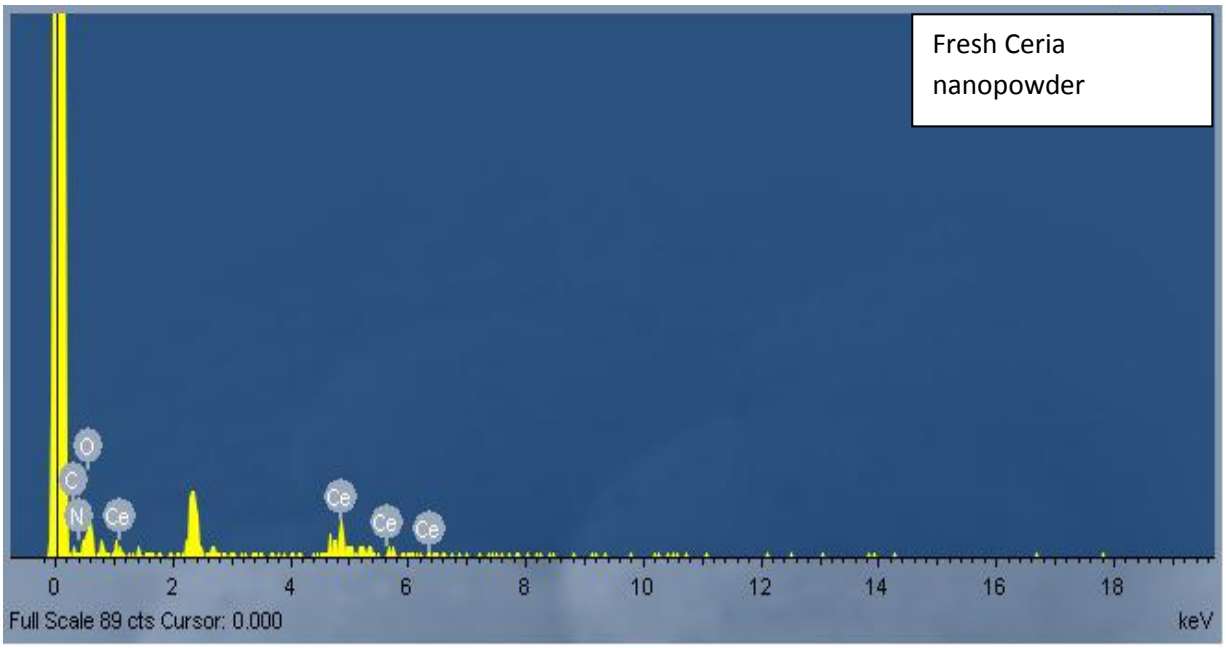


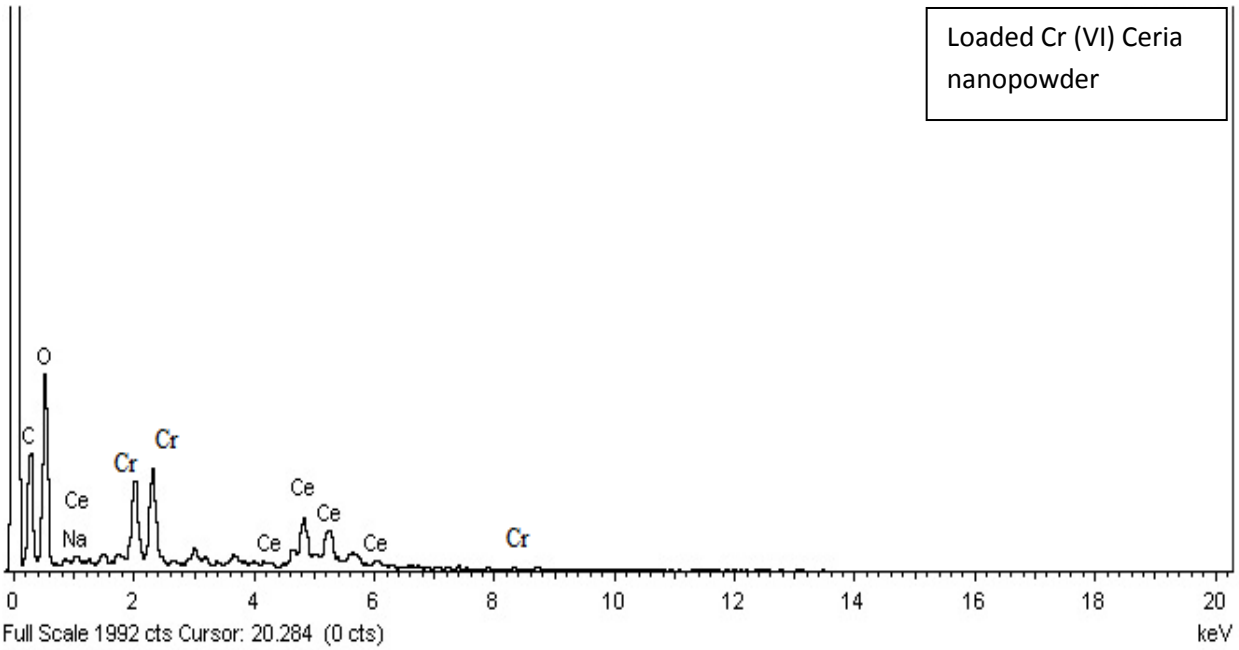
1a) Before Adsorption



1b) after adsorption

Figure 2: EDAX analysis of the ceria nanopowder.





3.1.2 BET study:

BET surface area study of the material is done through nitrogen adsorption technique and it is found that the material is having a high surface area (Table 4), the specific surface area of the material is not incorporated because the results of the analysis are awaited.

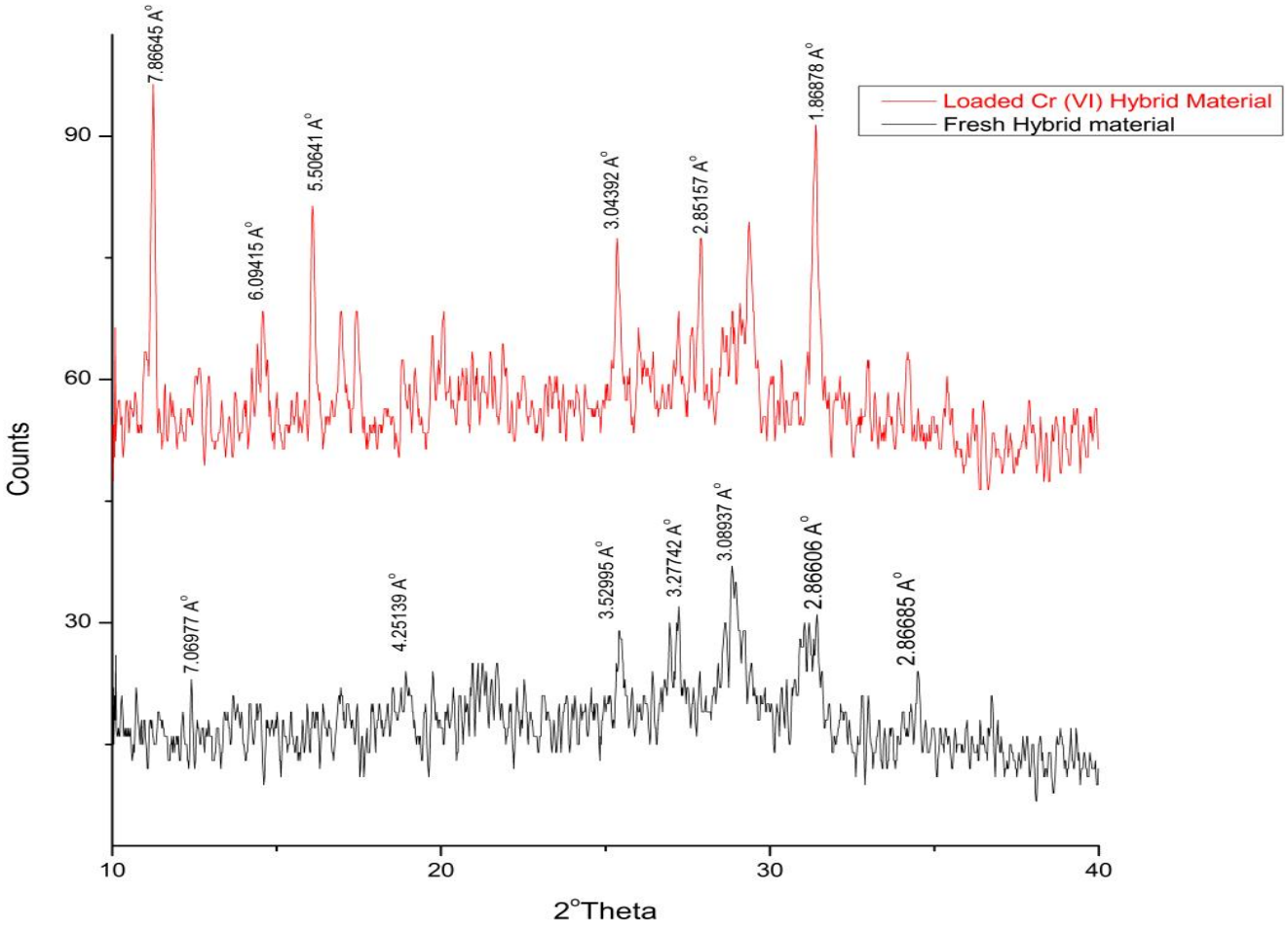
Table-4: BET-Isotherm report of the Ceria nanopowder

Property	Method	Ce-Nanopowder
Specific surface area (m^2/g)	Nitrogen adsorption	awaited
Pore Volume (Cm^3/g)	Nitrogen adsorption	awaited
pore diameter	Nitrogen adsorption	awaited

3.1.3. XRD study

Powdered XRD of the material was obtained by using PHILIPS X'PERT X-Ray Diffractometer with Cu kα radiation(35 kv and 30 mA) at a scan rate of 20/min and was analysed using standard software provided with the instrument. The XRD pattern of the sample is presented in (Figure. 3); few sharp peaks were obtained after loading hexavalent chromium, indicating the sample was partially amorphous in nature. XRD was analysed using standard expert high score. The material can be compared on the basis of d-spacing of 7.06977 [A°] at, 2 theta13° is found with slight increase in the d spacing of loaded hybrid material of d spacing 7.86645 [A^{o}], before adsorption it is supported by the JCPDES file number 28-0055.

Figure 3: XRD patterns of Ceria nanopowder

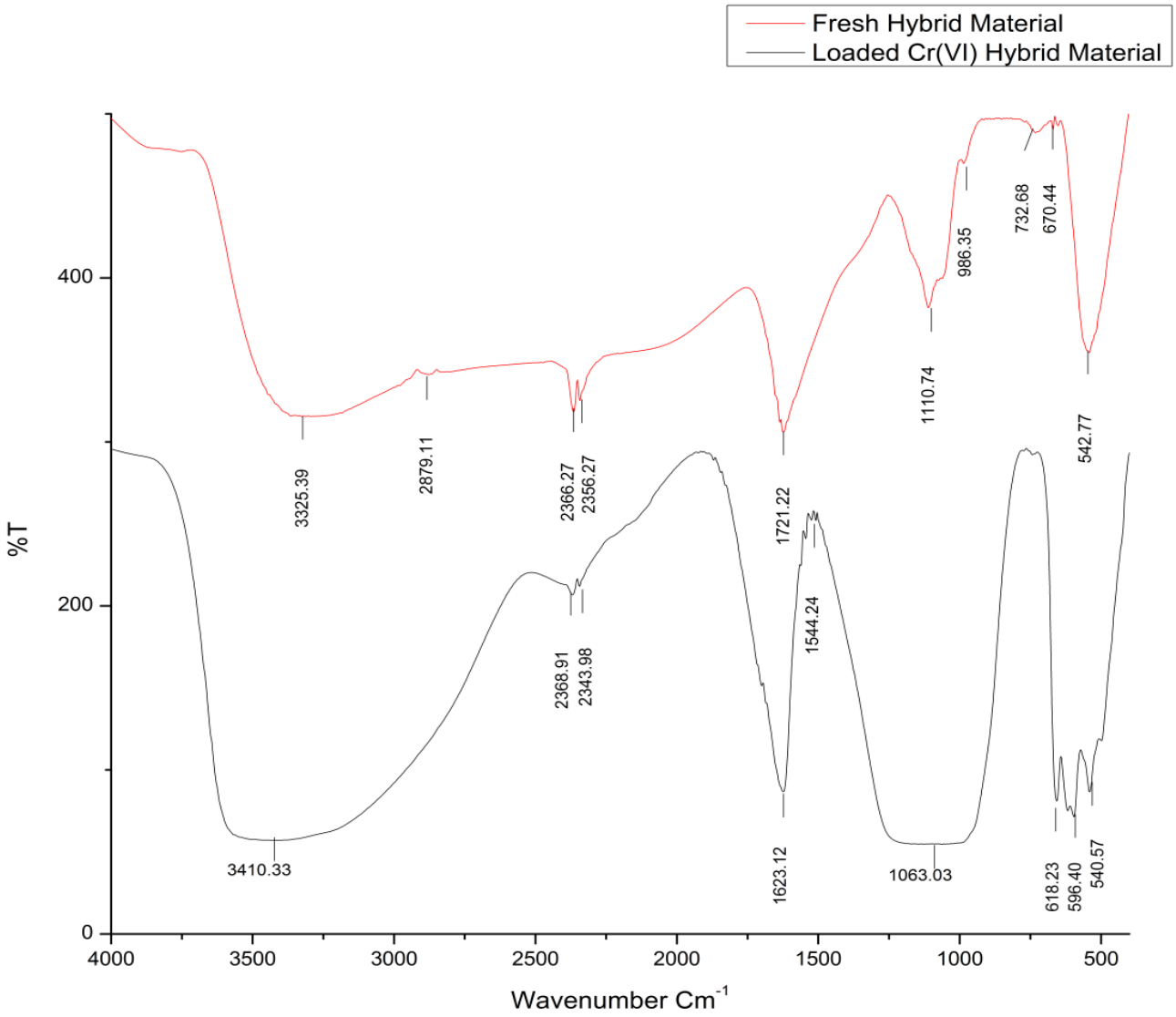


3.1.4. FTIR of ceria nano study

FTIR study of the sample was carried out (Figure. 4) in order to know the presence of different groups and structures in the material. The presence of band at 3325.39 cm^{-1} of fresh nano material is due to bonded -OH groups, which indicates the presence of initial water of crystallization. Further, the presence of a peak at 3410.33 cm-1 in loaded material is due to overlapping of OH group with NH_2 group. The peak at 2366.27 cm^{-1} and 2356.27 cm^{-}

[1]isshifted in loaded material towards 2368.91cm^{-1} and 2343.98cm^{-1} is due to bonding of the chromate anion (CrO_4^{2-}). The peak at 670.44 cm $^{-1}$ and 542.77 cm $^{-1}$ in Ceria nanopowder is assigned to metal- oxygen bonding is further shifted after adsorption towards 596.40 cm^{-1} and 540.57 cm^{-1}.

Figure 4: FTIR pattern of Ceria-Nanopowder before adsorption and after adsorption



3.1.5 Particle Size Data:

From particle size data, it is found that the size of Ceria nanopowder is in the nano order range. The size of Ceria nanopowder is 665.4 nm. The 300^0 calcined sample is 764.9 nm and 500^0 calcined sample has 252.0 nm sizes.

Table-5: Particle size data of Ceria Nanopowder

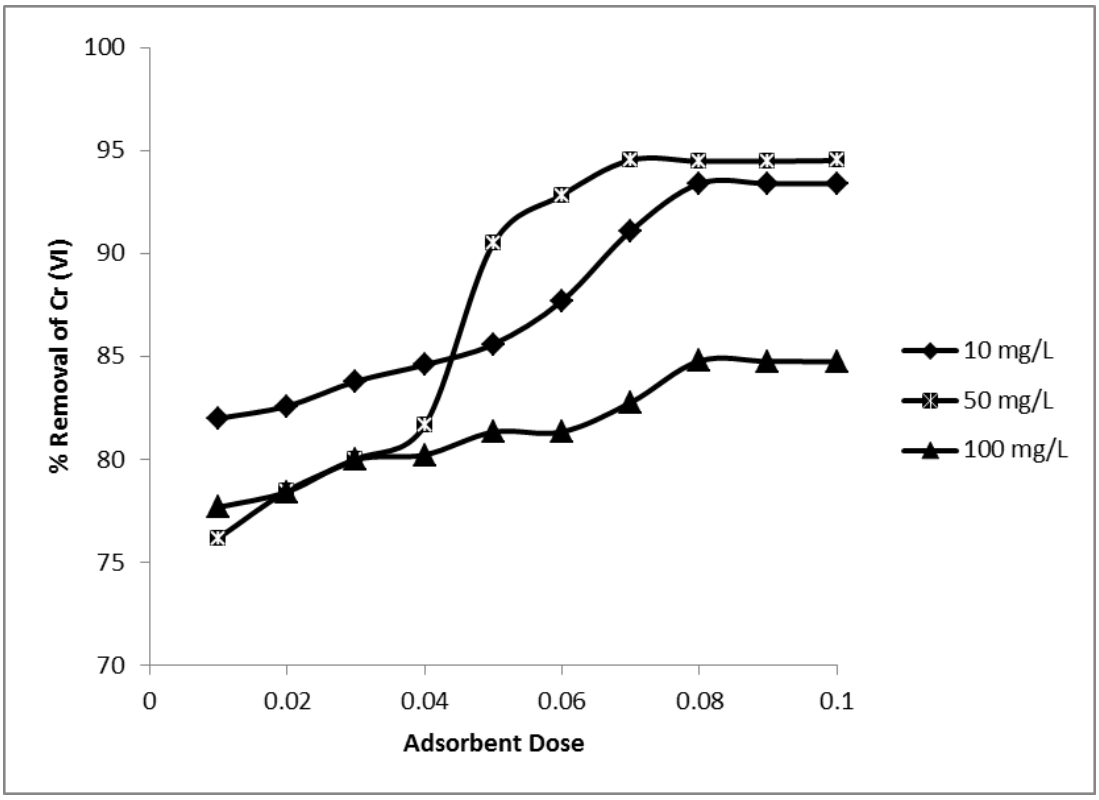
Sample	Size (r.nm)	Width (r.nm)
Ceria Nano	665.4	118.9
Ce Nano (300^0) calcined	764.9	120.7
Ce Nano (500^0) calcined	252.0	37.94

3.2 Batch Study of Ceria Nanopowder

3.2.1. Effect of Adsorbent Dose on the Removal of hexavalent chromium from Contaminated Water

The effect of adsorbent dose on the removal of chromium (VI) is studied in neutral condition (pH 7), at ambient temperature (28±2 ^oC) and contact time of 30 minute for initial chromium (VI) concentration of 10mg/L, 50mg/L and 100mg/L. The results are shown in (Figure 5). It is evident from the (Figure 5) that the removal of hexavalent chromium raises from 82 % to 93.34 %, 76 % to 94 % and 77 % 84 % for 0.01 – 0.1 g/100ml of Ceria nanopowder as a hybrid material respectively with initial chromium (VI) concentration of 10mg/L, 50mg/L and 100mg/L. It is observed that after dosage of 0.07mg/100 ml, there is no significant change in percentage of removal of hexavalent chromium. It may be due to the overlapping of active sites at higher dosage and conglomeration of the exchanger. So, 0.07mg/100ml is considered the optimum dose and is used for further study.

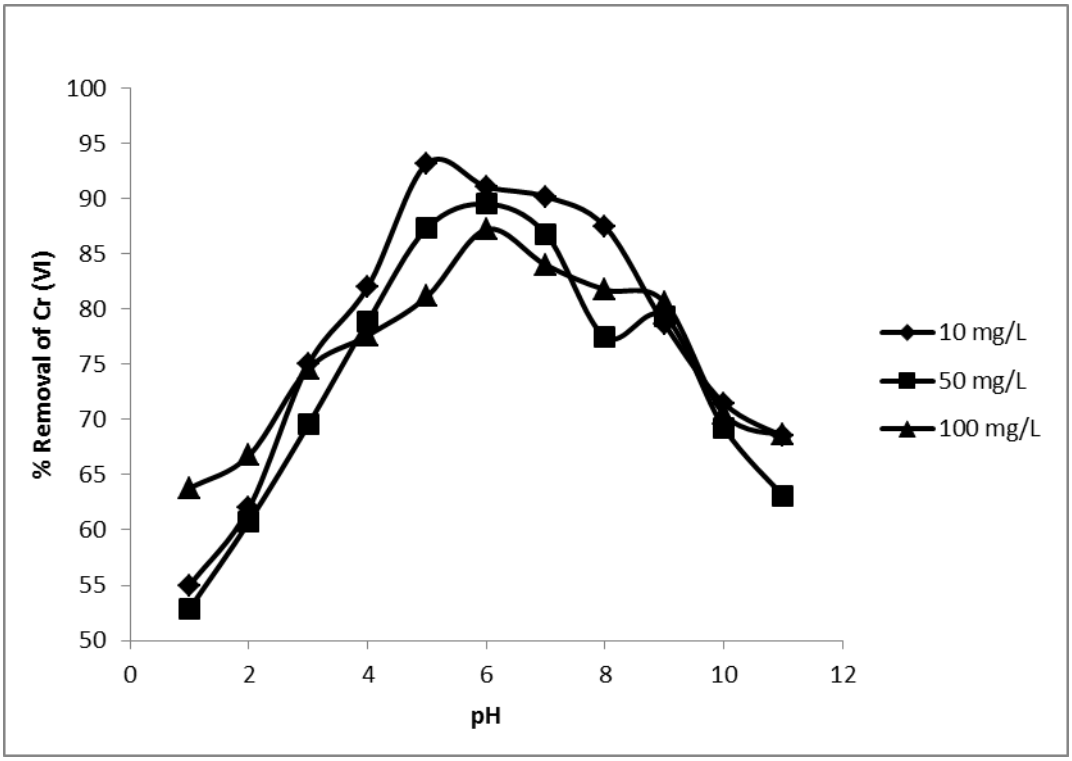
Figure 5: Effect of adsorbent dose on the removal of Cr (VI) using Ceria Nanopowder



3.2.2. Effect of pH on the Removal of hexavalent chromium from Contaminated Water

Percentage removal of hexavalent chromium at different pH is studied in batch mode using 0.07 mg of adsorbent in 100 ml aqueous solution, at ambient temperature (25±2 ^{o}C) , contact time of 50 minute for initial chromium (VI) concentration of 10mg/L, 50mg/L, and 100mg/L. The results are presented in (Figure 6). The pH of the solution after adsorption is measured and is found to increase or decrease slightly without any regular trend. It is evident from the graph that there is removability at pH 5 and to pH 8 almost 93 % removals and the highest removal was achieved at pH 6.The decrease of chromium (VI) uptake at alkaline pH could be due to competition for active sites by excessive amount of hydroxyl ions which further competes with $Cr_2O_7^{2-}$ ions present in the water.

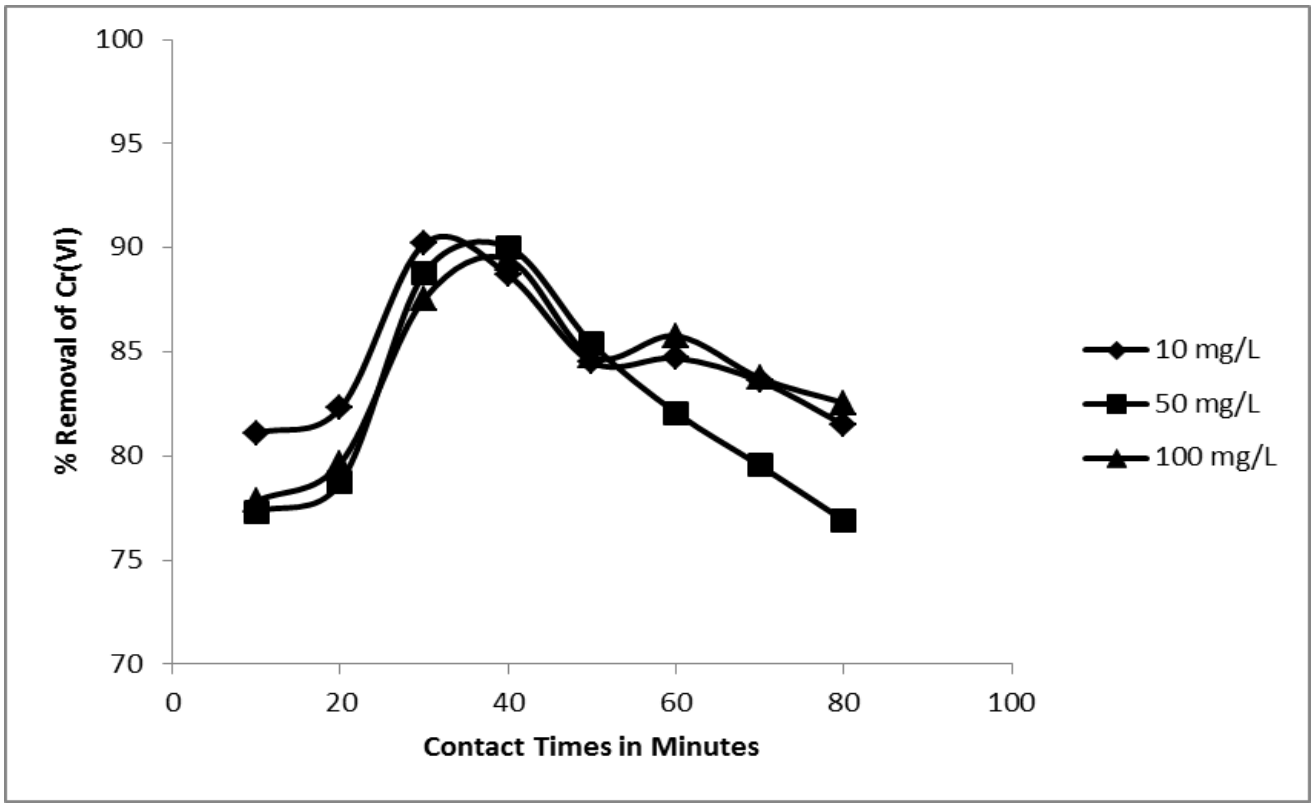
Figure 6: Effect of pH on the Removal of hexavalent chromium from Contaminated Water using Ceria Nanopowder



3.2.3. Effect of contact times on the removal of hexavalent chromium from contaminated water

Batch study of chromium (VI) at different contact time is studied for initial chromium (VI) concentration of 10mg/L, 50mg/L and 100mg/L at pH 7 and adsorbent dose of 0.07 mg/L keeping all other parameters constant. The result is represented in (Figure 7). It is understand from the (Figure 7) that more than 90 % removal takes place within 30 min and equilibrium is reached after 30 min. The alteration in the rate of removal might be due to the fact that initially all adsorbent sites are unused and also the solute concentration gradient is high. Later the chromium (VI) uptake rate by adsorbent is decreased provocatively, due to the decrease in the number of vacant adsorption sites present in the nano material as well as decreases in hexavalent concentration.

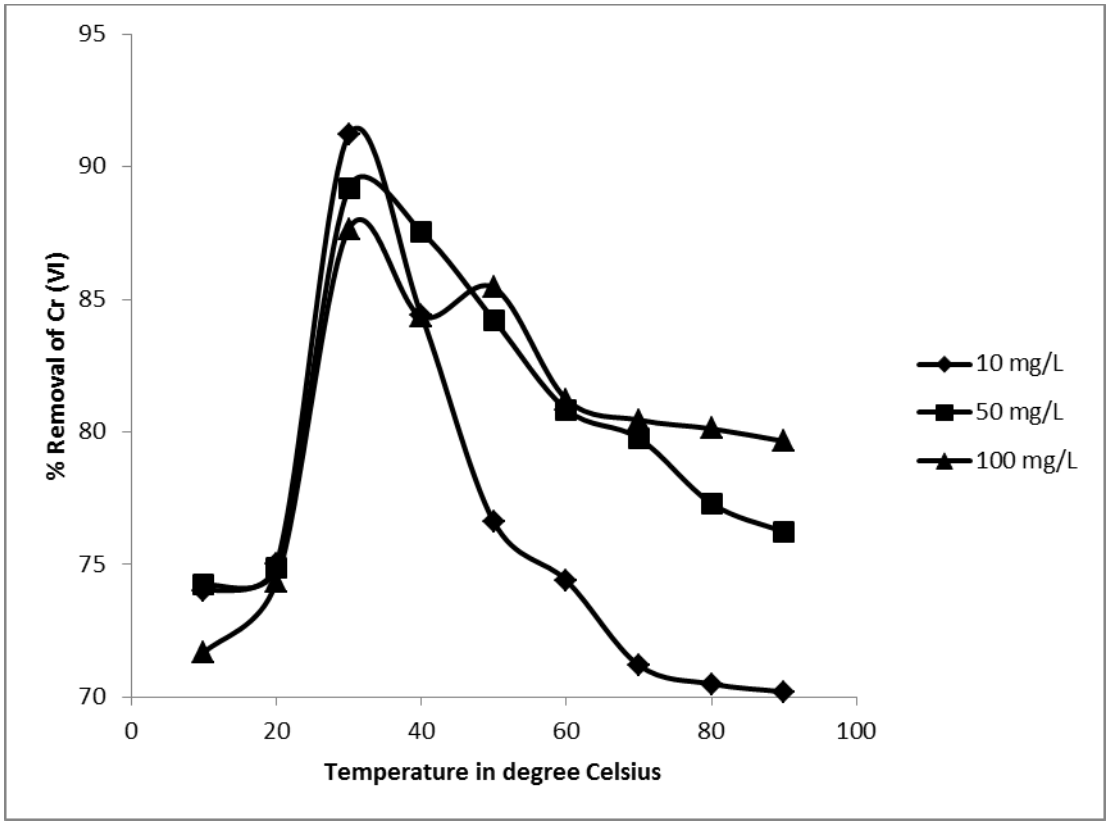
Figure 7: effect of contact time on Percentage removal of hexavalent chromium using Ceria Nanopowder



3.2.5. Effect of Temperature on percentage removal of chromium (VI) from contaminated water

The importance of temperature on the adsorption of chromium (VI) with initial concentration 10mg/L, 50 mg/L and 100 mg/L is considered using optimum adsorbent dose (0.07 mg/100mL) and at contact time of 50 minutes. The results are represented as percentage removal of hexavalent chromium) versus temperature (Figure 8). The percentage removal of chromium (VI) with initial concentration10mg/L, increased from 74 % to 91%, for 50 mg/L, increased from 74 %to 89 % and for 100 mg/L, increased from 71 % to87% for 25 to 45° C temperatures respectively. From the (Figure 8) that, at the temperature 30^{o} Celsius the removal was almost 91 % and with increase in temperature the percentage removal decreases slowly and reached almost 88 %.

Figure 8: Effect of temperature on the removal of hexavalent chromium using Ceria Nanopowder

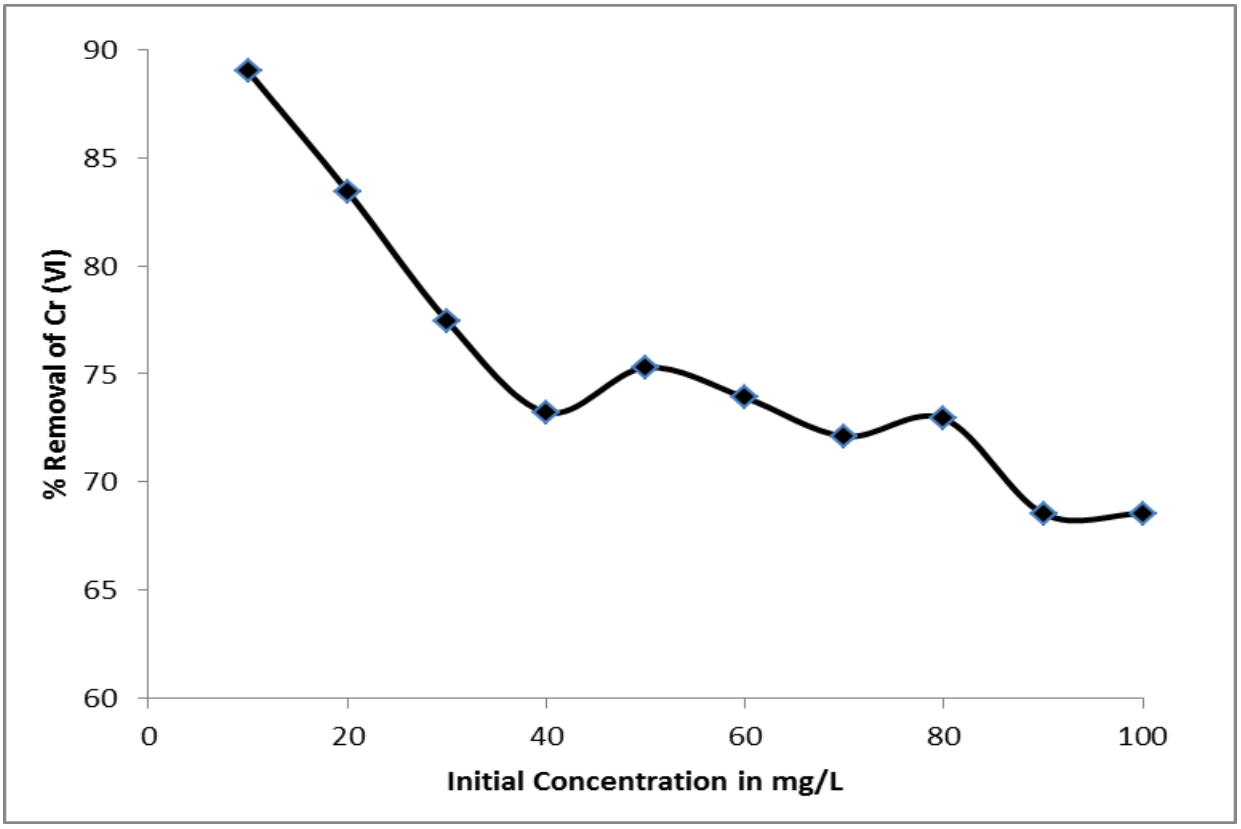


3.2.6. Effect of initial Hexavalent chromium concentration

The adsorption of hexavalent chromium onto Ceria Nanopowder is calculated by varying initial hexavalent chromium concentration using optimum adsorbent dose (0.07mg/100ml) at ambient temperature (25±2 ^{o}C) and contact time of 30 min. The results are suggested in graphical form as percentage removal versus initial hexavalent chromium concentration in (Figure 8).The initial chromium (VI) concentration is increased from 10mg/L to 100 mg/L and the corresponding removal gradually decreases from 89 % to 68 %. It is observed from the (Figure 8) that, there is a decrease in removal percentage with increase in initial

chromium (VI) concentration due to the fact that at greater adsorbate concentration, the free sites available approaches overload at later stage with increase in the concentration of the solution..

Figure 11: percentage removal of hexavalent chromium using Ceria Nanopowder versus initial Cr (VI) concentration



4. CONCLUSION

From the overall studies of chromium adsorption, a few important observations are obtained. The synthesized material is in powdered form. The hybrid material is in the nano order range which is evident from the particle size analysis. The material is found to be partially amorphous in nature as marked in the XRD data. From SEM-EDAX report it is found that the material is nano fibre and do not have identifiable pores. From BET, the specific surface area of the material is not incorporated because the results of the analysis are awaited.. The removal efficiency of the hexavalent chromium from water is done by using this material is conducted by varying the variable parameters like contact time, pH, amount of adsorbent and temperature and initial concentration. The hybrid material was found to have a maximum efficiency for the removal of hexavalent chromium with 86 to 88%, pH at 7, adsorbent dose of 0.07gm and temperature of 28±2°C and initial concentration of 10 ppm. The structure of the material is confirmed by the FTIR data which shows the presence of metal-oxygen bonding. From all the above observations it may be concluded that the material is suitable to act as adsorbent for the removal chromium (VI) from water and also it requires a further study.

4.1. Future Work:

- The kinetic study of the hybrid material and its detail characterization.
- To study the validity of various isotherm models.
- To study the removal of other heavy metal.
- To study the effect of competitive anion present in the removal efficiency of chromium (VI).
- Further practical application of the material.
- To remove all the oxidation states of chromium.
- The formulation of a working model, which can be implemented in field studies incorporating all the data.

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